Synthesis of High-Quality Vertically Aligned Carbon Nanotubes on Bulk Copper Substrate for Thermal Management

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***Abstract*—Vertically aligned carbon nanotubes (VACNTs) grown on bulk copper substrate are of great importance for real-life commercial applications of carbon nanotubes (CNTs) as thermal interface materials in microelectronic packaging. However, their reproducible syntheses have been a great challenge so far. In this study, by introducing a well-controlled conformal Al_2O_3 support layer on the bulk copper substrate by atomic layer deposition, we reproducibly synthesized VACNTs of good alignment and high quality on the copper substrate. The alignment and the quality were characterized by scanning electron microscope, transmission electron microscope, and Raman spectroscopy. The key roles of the conformal Al_2O_3 support layer by atomic layer deposition are discussed. This progress may provide a real-life VACNT application for thermal management.**

***Index Terms*—Carbon nanotube, chemical vapor deposition (CVD), thermal interface materials.**

I. Introduction

CARBON nanotubes (CNTs) have attracted extensive attention due to their outstanding electrical, thermal, and mechanical properties, and their wide range of potential applications [1]–[6]. One promising application of CNTs in microelectronic packaging is to use vertically aligned carbon nanotubes (VACNTs) as thermal interface materials (TIMs) to enhance heat dissipation [7]–[13]. For a typical VACNT TIM assembly, a VACNT layer is synthesized on a typical growth substrate such as silicon and then brought into contact with a mating substrate by, for example, compression force [7], [10], [12], solder anchoring [14], or chemical bonding [15]. Although VACNT synthesis on silicon as the growth substrate has been widely investigated, direct synthesis of a VACNT layer on the backside of a silicon device is not compatible with a current front-end semiconductor fabrication process due to the high temperature (typically $> 650\,^{\circ}\mathrm{C}$) required for VACNT syntheses via chemical vapor deposition (CVD). Thus, a silicon substrate is not the growth substrate of choice for real-life VACNT TIM applications; instead, VACNT synthesis on a bulk copper substrate, i.e., a copper lid, is preferred [16], [17], as briefly illustrated in Fig. 1. A few papers have reported VACNT syntheses on various metal substrates, however, the direct VACNT synthesis on a bulk copper substrate is still a great challenge [18]–[25]. Wang *et al.* developed a process to grow VACNTs on a copper foil surface by water-vapor-assisted CVD [26]. However, the quality and the structure of the "VACNTs" on copper were not described clearly. Recently, Yin *et al.* reported growing multiwalled CNTs on an oxygen-free copper substrate, however, with a poor CNT alignment [27]. Implementation of VACNTs grown on copper for thermal management was reported by Fisher's research group [7], [10]. A trilayered catalyst structure (6-nm Ni/10-nm Al/30-nm Ti) deposited on a copper substrate/foil was used to grow VACNTs by a microwave plasma CVD process. Nevertheless, the VACNTs in these two references exhibited different average diameters, diameter distributions and CNT coverage on the growth substrates, even though the same synthetic conditions were used. It has turned out that high reproducibility of VACNT growth on bulk copper substrates is still quite challenging. Besides, fundamental understanding of the roles of the support layers underneath the catalyst layer during the VACNT synthesis on copper is still not clear. Thus, a reproducible process of synthesizing high-quality VACNTs on bulk copper substrates, coupled with its fundamental understanding, is urgently needed. In this paper, we report a remarkable progress on fast synthesis of high-quality VACNTs on bulk copper substrates through a common thermal CVD process.

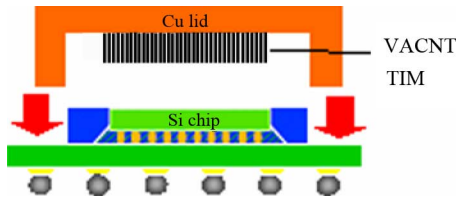

Fig. 1. Conceptual illustration of the vertically aligned carbon nanotubes grown on a copper lid surface as TIM for heat dissipation in microelectronic packaging.

II. Experimental

Copper plates (1×1 cm^2) were purchased from Speedy Metals Inc. Copper substrates as received were designated as nonpolished copper in this work and had an average roughness $R_a = 0.9 - 1.2\ \mu$m and a peak-to-valley height $R_z = 7.3 - 8.9\ \mu$m. Well-polished copper had a

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$R_a = 0.35 - 0.42\ \mu\mathrm{m}$ and a $R_z = 3.5 - 3.9\ \mu\mathrm{m}$. R_a and R_z values were measured on a profilometer (Tencor KLA, P15 OF). Copper substrates were cleaned with acetone and isopropanol sequentially, and dried in nitrogen (Airgas) at room temperature. A thin layer of $\mathrm{Al_2O_3}$ was used as a support layer on the copper substrate for VACNT synthesis. In order to study the influence of the quality of the $\mathrm{Al_2O_3}$ support layer on VACNT synthesis, two different approaches of $\mathrm{Al_2O_3}$ deposition were studied and compared. $\mathrm{Al_2O_3}$ deposited by e-beam evaporation was conducted at a vacuum of $7.8 \times 10^{-7} - 1.1 \times 10^{-6}$ Torr, with a deposition rate of 0.4–0.5 Å/s. Atomic layer deposition (ALD) of $\mathrm{Al_2O_3}$ layers were carried out using $\mathrm{Al(CH_3)_3}$ (trimethyl aluminum, TMA, Sigma-Aldrich) and distilled water alternatively entrained in nitrogen (Airgas) carrier flow. Exposure time in the TMA and the water vapors was 10 s each. The chamber pressure and the chamber temperature were kept at ~ 1.0 Torr and 250 °C, respectively. A thin layer of iron was chosen as the catalyst for CNT synthesis. E-beam evaporation of the iron catalyst (3–3.5 nm) on top of an $\mathrm{Al_2O_3}$ support layer was conducted in a vacuum of $4.5 \times 10^{-7} - 7.5 \times 10^{-7}$ Torr, with a deposition rate of 0.1–0.2 Å/s. For the sake of comparison, VACNTs were also synthesized on silicon and surface oxidized silicon substrates with an $\mathrm{Al_2O_3}$ support layer and a Fe catalyst layer. Surface oxidation of the silicon substrates was carried out in a three-zone furnace using a conventional wet oxidization process.

CVD synthesis of VACNTs was carried out at 750 °C, with the gas flow rate ratio as: $\mathrm{Ar/H_2/C_2H_4} = 380/150/150$ standard cubic centimeter per minute. A trace amount of water was introduced into the chamber for accelerating CNT growth and simultaneously removing surface amorphous carbon [28]. Scanning electron microscope (SEM) images were obtained with a JEOL 1530 equipped with a thermally assisted field emission gun operating at 10 keV. Transmission electron microscope (TEM) images were captured in JEOL 4000EX. CNT Raman spectra were collected on top of the VACNT layers on a CRM-200 confocal Raman microscope (Witec, Inc). The excitation laser was an argon-ion laser with a wavelength of 514.5 nm. Atomic force microscopy was performed in a Dimension 3100 from Veeco Instruments operating in a taping mode in air.

III. Results and Discussion

Here we have synthesized VACNTs on various substrates, including copper plates (well-polished and non-polished), bare silicon wafers and surface-oxidized silicon wafers. Experimental results are briefly listed in Table I. We have observed and summarized three important phenomena: 1) a thin $\mathrm{Al_2O_3}$ support layer (5–20 nm) deposited by e-beam evaporation fails to grow VACNTs on either well-polished or non-polished copper substrates; 2) ALD, compared with e-beam evaporation, is a much better approach of making an efficient $\mathrm{Al_2O_3}$ support layer on the copper substrates for VACNT growth; 3) an ultra-thin $\mathrm{Al_2O_3}$ layer (5 nm) deposited by ALD is efficient for VACNT growth on a surface-oxidized silicon substrate but it is ineffective on a bare silicon substrate. The quality of the $\mathrm{Al_2O_3}$ support layer and its actual thickness are the key points that account for the different results and they all depend on the $\mathrm{Al_2O_3}$ deposition method and the surface roughness of the growth substrate.

TABLE I
Brief Summary of the Experimental Results of VACNT Syntheses on Various Substrates With Varied $\mathrm{Al_2O_3}$ Deposition Methods

Substrates	Al_2O_3 preparation	Al_2O_3 thickness [nm]	VACNT thicknesss [μm]
Non-polished copper plates	e-beam	5-30	--[b]
	ALD	5, 10	--
		15, 20	< 50
		25, 30	> 100
Well-polished copper plates	e-beam	5-20	--
		25, 30	< 50
	ALD	5	--
		10	< 50
		15, 20, 25	> 100
Si	e-beam	5, 10	--
		15, 20	< 500
Si	ALD	5	--
		10	> 100
		15	> 800
		20, 25	> 1200
SiO_2/Si	ALD	5, 10, 20	> 1800

a) The average VACNT array thickness after 20-min growth on a 1-cm^2 substrate under the same CVD conditions.
b) An uniform VACNT array could not be made.

A. Discontinuity of the $\mathrm{Al_2O_3}$ Support Layer By E-Beam Evaporation

$\mathrm{Al_2O_3}$ support layers of 10–15 nm thick have been used to accelerate VACNT growth due to their ability to decompose hydrocarbons and the interfacial interactions between $\mathrm{Al_2O_3}$ and iron nanoparticles during the CVD syntheses of VACNTs [29]–[31]. Generally, the literature describe the conditions for the formation of an $\mathrm{Al_2O_3}$ deposit layer on a target substrate by e-beam evaporation; however, the continuity of the deposit has rarely been mentioned. During an e-beam evaporation process, a continuous deposit layer forms on a substrate surface through nucleation and growth steps. At an early stage of deposition, heterogeneous nucleation may become rate controlling. This nucleation mechanism leads to isolated aggregates of condensate on the substrate when the deposit layer is thin [32]. This discontinuity is briefly discussed by de los Arcos *et al.* [33]. In fact, the discontinuity of the deposit is the right reason why a thin layer of gold deposit on a bare silicon surface by e-beam evaporation was recently employed to selectively etch silicon wafers [34]. In our study, for the $\mathrm{Al_2O_3}$ deposition on the commercial copper substrate, the poor wetting of $\mathrm{Al_2O_3}$ on copper together with the surface roughness and impurity of the copper substrate assists the heterogeneous nucleation and makes a thin $\mathrm{Al_2O_3}$ deposit discontinuous. A continuous deposit forms only when the growing layer thickens enough for the aggregate to impinge on each other [32]. Therefore, when the $\mathrm{Al_2O_3}$ deposit layer

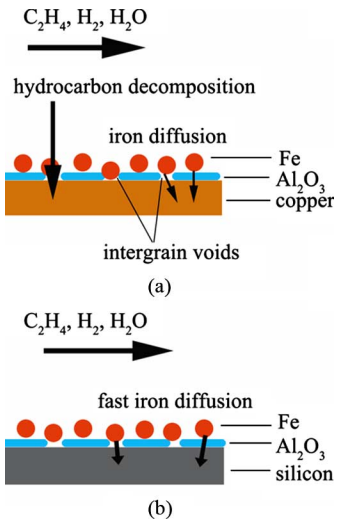

Fig. 2. Illustrations of an ineffective support layer on a copper or a silicon surface during a CVD process.

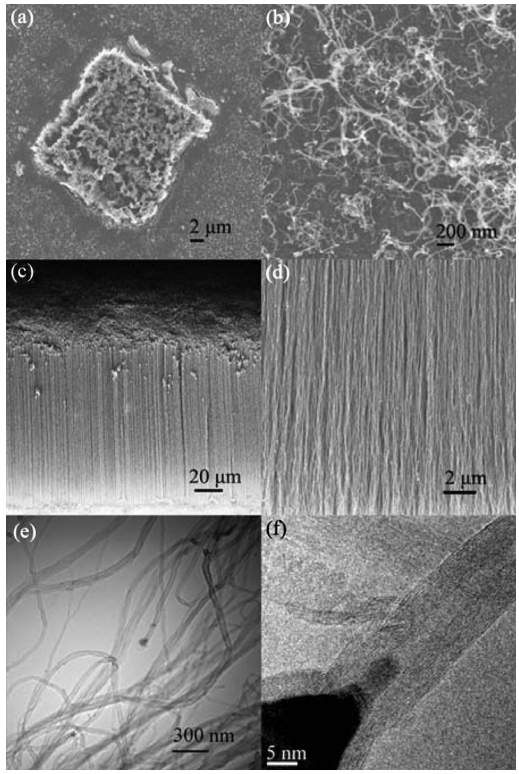

Fig. 3. SEM images of the surface status, (a) and (b), of a nonpolished copper substrate after VACNT synthesis failure and the side views, (c) and (d), of the VACNTs grown on a nonpolished copper substrate. The copper substrate in (a) and (b) was deposited with 30 nm Al_2O_3 and 3.5 nm iron by sequential e-beam evaporation; the copper substrate in (c) and (d) was deposited with 20 nm Al_2O_3 by ALD and 3 nm iron by e-beam evaporation sequentially. (e) and (f): TEM images of the CNTs in (c) and (d).

is too thin to become continuous, isolated nanoaggregates are formed [33], [35]. In this case, the bottom copper surface is partially exposed to the top iron catalyst and/or the carbon source at the inter-grain voids during the CVD process, as illustrated in Fig. 2(a), and the VACNT synthesis fails. Fig. 3(a) and (b) shows the surface status of a nonpolished copper substrate (with 30 nm Al_2O_3 and 3.5 nm Fe deposited by sequential e-beam evaporation) after the CVD process of CNT synthesis.

There are at least two reasons that account for the synthesis failure. First, copper deactivates the CNT growth. Pure copper does not catalyze decomposition of hydrocarbons as the interaction of the hydrocarbons with the copper surface does not lead to the rupture of the carbon-carbon bonds [36]. Additionally, solubility of carbon in solid copper is extremely low [37], [38]. Thus, when the copper surface is exposed to the top iron particles during the CVD process, the local copper-rich catalyst composition is capable of decomposing hydrocarbons, however, without giving rise to ordered graphitic structures [36], [39]. Second, iron diffuses into copper when the iron particles are in contact with the copper surface at the intergrain voids [32]. Iron is known to tend to diffuse into a bare silicon substrate (diffusion coefficient $D \sim 10^{-7}$ cm^2/s at 1000 K) and to form chemical compound with silicon. Such diffusion makes the VACNT growth directly on a bare silicon substrate almost impossible in the absence of a surface oxidation layer as the barrier layer due to depletion or intoxication of the iron catalyst [40]–[43]. Cao *et al.* [40] found that there was no detectable CNT growth on the silicon substrate when the surface oxidation layer was thinner than 6 nm because the thin porous oxidation layer was not effective in hindering iron diffusion into and reaction with the bottom silicon substrate. In our study, a thin Al_2O_3 deposit by e-beam evaporation is discontinuous and analogous to the thin porous silicon oxide in [43], as illustrated in Fig. 2(b). It is seen in Table I that a 5-nm-thick Al_2O_3 deposited by e-beam evaporation is not an effective support layer on a bare silicon wafer. Similarly, iron can easily diffuse into the copper substrate at the intergrain voids within the Al_2O_3 layer as well. The diffusion coefficient of iron in single-crystalline copper is higher than 10^{-12} cm^2/s at 1000 K, at least three orders of magnitude higher than that in silicon dioxide ($< 10^{-15}$ cm^2/s) [44], [45]. Moreover, it is expected that the polycrystalline copper that has been used in this study will experience rapid iron diffusion into the copper due to enhanced grain boundary diffusion rates and a concentration of iron at the grain boundaries.

A question arises as "how do we know whether a deposit layer is too thin to be continuous?" A 30-nm-thick Al_2O_3 deposited by e-beam evaporation is expected to be thick enough to be an effective support layer on the copper substrates; however, it fails on the nonpolished copper substrates. Since the thickness during e-beam evaporation is monitored by quartz crystal microbalance and calculated automatically with regard to a smooth surface like a polished silicon surface, surface roughness of the copper substrates plays a key role in determining the actual thickness of the deposit layer. As such, an increased surface roughness increases surface area and, consequently, reduces the actual deposit thickness. In this sense, a 30-nm-thick Al_2O_3 layer on a nonpolished copper substrate may still be too "thin;" while a smoother copper surface should make a difference. In Table I, we see that a 30-nm-thick Al_2O_3 layer is able to grow VACNTs on the well-polished copper, although the growth rate is small. We believe that the surface roughness probably accounts for the aforementioned poor reproducibility of the VACNT syntheses on copper substrates reported in the literature.

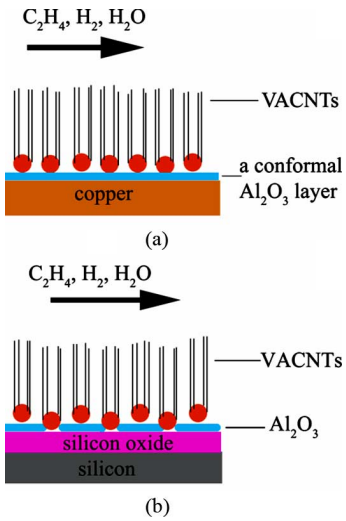

Fig. 4. Illustrations of an effective support layer on copper or silicon dioxide during a CVD process.

B. Dense Conformal Al_2O_3 Support Layer Deposited by ALD

Based on the discussion above, we postulate that a dense conformal Al_2O_3 support layer on the bulk copper substrate would be able to realize a reproducible CVD synthesis of VACNTs on copper substrates. To demonstrate this, we used ALD to prepare a well-controlled Al_2O_3 layer on a copper substrate. In comparison with e-beam evaporation, ALD, also known as atomic layer epitaxy, is a special modification of CVD with the capability of producing films with excellent conformality and precisely controlled thicknesses [46], [47]. In this study, ALD was carried out at 250 °C, with $Al(CH_3)_3$ and deionized water as the precursors. This process generates a uniform continuous support layer [47], [48] resulting in highly efficient VACNT synthesis on a copper substrate, as illustrated in Fig. 4(a). Furthermore, unlike the thickness monitoring during e-beam evaporation, the thickness of the Al_2O_3 layer deposited by ALD is accurate and insensitive to the surface roughness of copper substrates, as such, it guarantees a reproducible VACNT synthesis. It is shown in Table I that a relatively thin support layer on both of the copper surface, i.e., 10-nm- and 15-nm-thick Al_2O_3 on the polished and the nonpolished copper substrates, respectively, is able to support the VACNT growth. A thinner Al_2O_3 layer, i.e., 5 nm, is not effective while a thicker Al_2O_3 layer, i.e., 20 nm, results in a much higher VACNT growth rate. Fig. 3(c) and (d) shows a VACNT layer ($> 100\ \mu m$) grown on a nonpolished copper substrate with a 20-nm-thick Al_2O_3 layer deposited by ALD and a 3-nm-thick iron layer deposited by e-beam evaporation. A high density and a good alignment of CNTs are observed.

Additionally, in Table I, we have noticed that even when the support layer deposited by ALD is continuous, there is a lower limit on its effective thickness; a thicker support layer is more effective. This Al_2O_3 thickness-dependent growth of VACNTs on the copper and the silicon substrates is consistent with the results reported in [43], where it was reported a monotonic increase of CNT growth rate with increasing surface oxide thickness on a silicon substrate. A probable reason is the cracking

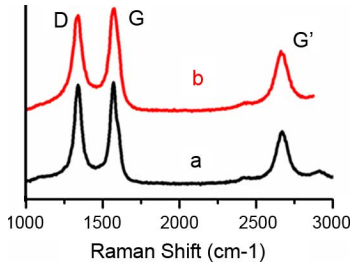

Fig. 5. Raman spectra of the VACNTs grown on SiO_2/Si (a) and on copper (b).

of a relatively thin Al_2O_3 layer and coarsening of the aggregates at high temperatures resulting in intergrain voids within the ALD deposit. In comparison, for VACNT growth on the surface-oxidized silicon wafers, an ultrathin (2.5–5 nm) support layer deposited by ALD is efficient. In this case, the surface SiO_2 layer (350 nm thick) serves as the main barrier layer, as illustrated in Fig. 4(b). Raman spectra of the VACNTs grown on the surface-oxidized silicon wafers and those on the copper substrates are shown in Fig. 5, indicating comparable VACNT qualities on both substrates, consistent with the TEM results in Fig. 3(e) and (f).

IV. Supplemental Information on AFM Characterizations

The surface of a 5-nm-thick Al_2O_3 layer on a bare silicon wafer surface prepared by e-beam evaporation is smooth, with a root-mean-square roughness of 0.196 nm, as shown in Fig. 6(a). Based on the nucleation-growth mechanism discussed above, the surface is expected to show lots of island-like features. However, the features are much smaller than the probe tip used and result in the large number of repeating patterns (artifacts) in the image. After a surface heat treatment for 1 h at 750 °C in Ar and H_2, the size of the surface features grew, as is clearly observed in Fig. 6(b). In comparison, the surface of an equally thick Al_2O_3 layer formed by ALD is even smoother and continuous [Fig. 6(c)]. Its root-mean-square roughness is only 0.155 nm, which is much smaller than that formed by e-beam evaporation. With the same heat treatment as above, the surface of the ALD-prepared Al_2O_3 layer retained its smoothness, showing features much smaller than the size of the probe tip (the artifacts in Fig. 6(d). Although there might be some difference between "discontinuity" and "surface roughness," we believe that for a 5-nm-thick coating, a higher surface roughness reflects discontinuity.

V. Conclusion

In summary, based on the fundamental understanding of e-beam evaporation, atomic layer deposition, VACNT growth mechanism during a CVD process, the surface roughness of the copper substrates and, copper–iron and copper–hydrocarbon interactions during the VACNT synthesis, we have realized a highly reproducible synthesis of VACNT TIMs on bulk copper substrates by a common CVD process. The synthesized VACNTs display good alignment and high quality. Overall, implementation of VACNTs as TIMs is complicated and still has a long way to go. The innovative work presented in this

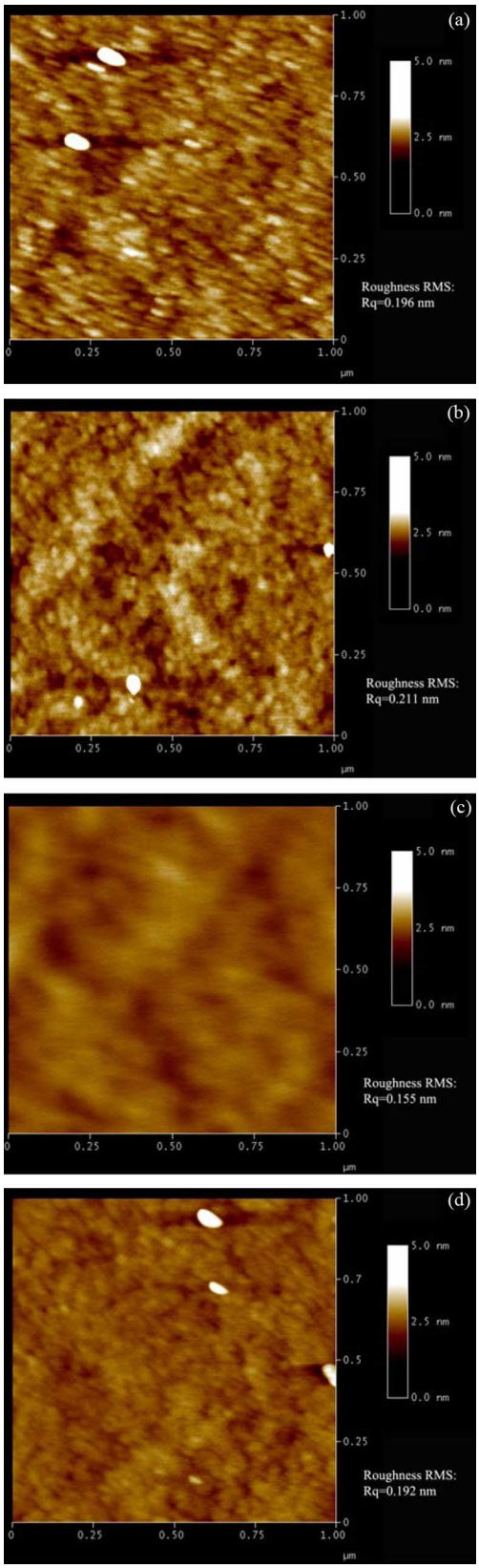

Fig. 6. AFM images of (a) a pristine 5-nm-thick Al_2O_3 layer on a bare silicon wafer surface by e-beam evaporation. (b) 5-nm-thick Al_2O_3 layer on a bare silicon wafer surface by e-beam evaporation after heat treatment for 1 h at 750°C in Ar and H_2. (c) Pristine 5-nm-thick Al_2O_3 layer on a bare silicon wafer surface by ALD. (d) A 5-nm-thick Al_2O_3 layer on a bare silicon wafer surface by ALD after heat treatment for 1 h at 750 °C in Ar and H_2.

paper aims at addressing the issue of VACNT synthesis on heat spreaders and pushing VACNT TIMs a step forward toward their potential commercial applications. More efforts are needed to increase CNT packing density on the growth substrate while maintaining the high flexibility of the CNT array, which requires further improvement of CNT quality and purity, and also the capability of finely tuning CNT diameter. A second issue, which is also the main challenge of CNT applications in many fields, is the anchoring and transport properties at the interface between the CNTs and the mating substrate, i.e., the backside of a silicon chip. To address this issue, a proper interface design based on fundamental understanding of interfacial phenomenon is needed [17].

Note Added in Proof

Recently, the technique presented in this paper has been extended to synthesizing high-quality VACNTs on various bulk materials, such as silicon nitride, silicon carbide, aluminum oxide, aluminum nitride, stainless steel, etc. A provisional patent application for GTRC ID No. 4853 entitled "Fast growth of high-quality vertically aligned Carbon nanotubes on various substrates for applications as thermal interface materials" has been officially filed. By the time the manuscript was accepted, with optimized CVD process, the authors have been able to synthesize around 2-mm-thick VACNT arrays on bulk copper substrates.

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REFERENCES

[1] R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, "Carbon nanotubes—the route toward applications," *Science*, vol. 297, pp. 787–792, Aug. 2002.

[2] A. P. Graham, G. S. Duesberg, R. V. Seidel, M. Liebau, E. Unger, W. Pamler, F. Kreupl, and W. Hoenlein, "Carbon nanotubes for microelectronics?," *Small*, vol. 1, pp. 382–390, Apr. 2005.

[3] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, "Electrical conductivity of individual carbon nanotubes," *Nature*, vol. 382, pp. 54–56, Jul. 1996.

[4] E. Pop, D. Mann, Q. Wang, K. Goodson, and H. J. Dai, "Thermal conductance of an individual single-wall carbon nanotube above room temperature," *Nano Lett.*, vol. 6, pp. 96–100, Jan. 2006.

[5] Z. Liu, X. M. Sun, N. Nakayama-Ratchford, and H. J. Dai, "Supramolecular chemistry on water-soluble carbon nanotubes for drug loading and delivery," *Acs Nano*, vol. 1, pp. 50–56, Aug. 2007.

[6] S. J. Tans, A. R. M. Verschueren, and C. Dekker, "Room-temperature transistor based on a single carbon nanotube," *Nature*, vol. 393, pp. 49–52, May 1998.

[7] J. Xu and T. S. Fisher, "Enhancement of thermal interface materials with carbon nanotube arrays," *Int. J. Heat Mass Transfer*, vol. 49, pp. 1658–1666, May 2006.

[8] K. Kordas, G. Toth, P. Moilanen, M. Kumpumaki, J. Vahakangas, A. Uusimaki, R. Vajtai, and P. M. Ajayan, "Chip cooling with integrated carbon nanotube microfin architectures," *Appl. Phys. Lett.*, vol. 90, p. 123105, Mar. 2007.

[9] H. Huang, C. H. Liu, Y. Wu, and S. S. Fan, "Aligned carbon nanotube composite films for thermal management," *Adv. Mater.*, vol. 17, pp. 1652–1653, Jul. 2005.
[10] B. A. Cola, J. Xu, C. R. Cheng, X. F. Xu, T. S. Fisher, and H. P. Hu, "Photoacoustic characterization of carbon nanotube array thermal interfaces," *J. Appl. Phys.*, vol. 101, p. 054313, Mar. 2007.
[11] M. A. Panzer, G. Zhang, D. Mann, X. Hu, E. Pop, H. Dai, and K. E. Goodson, "Thermal properties of metal-coated vertically aligned single-wall nanotube arrays," *J. Heat Transfer-Trans. ASME*, vol. 130, p. 052401, May 2008.
[12] T. Tong, Y. Zhao, L. Delzeit, A. Kashani, M. Meyyappan, and A. Majumdar, "Dense, vertically aligned multiwalled carbon nanotube arrays as thermal interface materials," *IEEE Trans. Compon. Packag. Technol.*, vol. 30, pp. 92–100, Mar. 2007.
[13] S. Sihn, S. Ganguli, A. K. Roy, L. T. Qu, and L. M. Dai, "Enhancement of through-thickness thermal conductivity in adhesively bonded joints using aligned carbon nanotubes," *Composites Sci. Technol.*, vol. 68, pp. 658–665, Mar. 2008.
[14] L. B. Zhu, D. W. Hess, and C. P. Wong, "Assembling carbon nanotube films as thermal interface materials," in *Proc. IEEE Electron. Compon. Technol. Conf.*, 2007, pp. 2006–2010.
[15] W. Lin, Y. G. Xiu, H. J. Jiang, R. W. Zhang, O. Hildreth, K. S. Moon, and C. P. Wong, "Self-assembled monolayer-assisted chemical transfer of in situ functionalized carbon nanotubes," *J. Amer. Chem. Soc.*, vol. 130, pp. 9636–9637, Jul. 2008.
[16] W. Lin, K. S. Moon, and C. P. Wong, "A combined process of in-situ functionalization and microwave treatment to achieve ultra-small thermal expansion of aligned carbon nanotube/polymer nanocomposites: Toward applications as thermal interface materials," *Adv. Mater.*, vol. 21, pp. 2421–2424, Jun. 2009.
[17] W. Lin, R. W. Zhang, K. S. Moon, and C. P. Wong, "Molecular phonon couplers at carbon nanotube/substrate interface to enhance interfacial thermal transport," *Carbon*, vol. 48, pp. 107–113, Jan. 2010.
[18] B. A. Wang, X. Y. Liu, H. M. Liu, D. X. Wu, H. P. Wang, J. M. Jiang, X. B. Wang, P. A. Hu, Y. Q. Liu, and D. B. Zhu, "Controllable preparation of patterns of aligned carbon nanotubes on metals and metal-coated silicon substrates," *J. Mater. Chem.*, vol. 13, pp. 1124–1126, 2003.
[19] F. S. Xu, X. F. Liu, and S. D. Tse, "Synthesis of carbon nanotubes on metal alloy substrates with voltage bias in methane inverse diffusion flames," *Carbon*, vol. 44, pp. 570–577, Mar. 2006.
[20] W. Hofmeister, W. P. Kang, Y. M. Wong, and J. L. Davidson, "Carbon nanotube growth from Cu-Co alloys for field emission applications," *J. Vac. Sci. Technol. B*, vol. 22, pp. 1286–1289, May-Jun. 2004.
[21] M. Karwa, Z. Iqbal, and S. Mitra, "Scaled-up self-assembly of carbon nanotubes inside long stainless steel tubing," *Carbon*, vol. 44, pp. 1235–1242, Jun. 2006.
[22] S. Talapatra, S. Kar, S. K. Pal, R. Vajtai, L. Ci, P. Victor, M. M. Shaijumon, S. Kaur, O. Nalamasu, and P. M. Ajayan, "Direct growth of aligned carbon nanotubes on bulk metals," *Nature Nanotechnol.*, vol. 1, pp. 112–116, Nov. 2006.
[23] L. J. Gao, A. P. Peng, Z. Y. Wang, H. Zhang, Z. J. Shi, Z. N. Gu, G. P. Cao, and B. Z. Ding, "Growth of aligned carbon nanotube arrays on metallic substrate and its application to supercapacitors," *Solid State Commun.*, vol. 146, pp. 380–383, Jun. 2008.
[24] J. W. Liu, X. J. Li, and L. M. Dai, "Water-assisted growth of aligned carbon nanotube-ZnO heterojunction arrays," *Adv. Mater.*, vol. 18, pp. 1740–1744, Jul. 2006.
[25] M. K. Singh, P. P. Singh, E. Titus, D. S. Misra, and F. LeNormand, "High density of multiwalled carbon nanotubes observed on nickel electroplated copper substrates by microwave plasma chemical vapor deposition," *Chem. Phys. Lett.*, vol. 354, pp. 331–336, Mar. 2002.
[26] H. Wang, J. Y. Feng, X. J. Hu, and K. M. Ng, "Synthesis of aligned carbon nanotubes on double-sided metallic substrate by chemical vapor deposition," *J. Phys. Chem. C*, vol. 111, pp. 12617–12624, Aug. 2007.
[27] X. W. Yin, Q. L. Wang, C. G. Lou, X. B. Zhang, and W. Lei, "Growth of multi-walled CNTs emitters on an oxygen-free copper substrate by chemical-vapor deposition," *Appl. Surface Sci.*, vol. 254, pp. 6633–6636, Aug. 2008.
[28] L. B. Zhu, Y. Y. Sun, D. W. Hess, and C. P. Wong, "Well-aligned open-ended carbon nanotube architectures: An approach for device assembly," *Nano Lett.*, vol. 6, pp. 243–247, Feb. 2006.
[29] C. Mattevi, C. T. Wirth, S. Hofmann, R. Blume, M. Cantoro, C. Ducati, C. Cepek, A. Knop-Gericke, S. Milne, C. Castellarin-Cudia, S. Dolafi, A. Goldoni, R. Schloegl, and J. Robertson, "In-situ X-ray photoelectron spectroscopy study of catalyst-support interactions and growth of carbon nanotube forests," *J. Phys. Chem. C*, vol. 112, pp. 12207–12213, Aug. 2008.
[30] L. B. Zhu, J. W. Xu, F. Xiao, H. J. Jiang, D. W. Hess, and C. P. Wong, "The growth of carbon nanotube stacks in the kinetics-controlled regime," *Carbon*, vol. 45, pp. 344–348, Feb. 2007.
[31] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, "Water-assisted highly efficient synthesis of impurity-free single-waited carbon nanotubes," *Science*, vol. 306, pp. 1362–1364, Nov. 2004.
[32] C. F. Powell, J. H. Oxley, J. Johan, and M. Blocher, *Vapor Deposition*. New York: Wiley, 1966.
[33] T. de los Arcos, F. Vonau, M. G. Garnier, V. Thommen, H. G. Boyen, P. Oelhafen, M. Duggelin, D. Mathis, and R. Guggenheim, "Influence of iron-silicon interaction on the growth of carbon nanotubes produced by chemical vapor deposition," *Appl. Phys. Lett.*, vol. 80, pp. 2383–2385, Apr. 2002.
[34] Y. H. Xiu, S. Zhang, V. Yelundur, A. Rohatgi, D. W. Hess, and C. P. Wong, "Superhydrophobic and low light reflectivity silicon surfaces fabricated by hierarchical etching," *Langmuir*, vol. 24, pp. 10421–10426, Sep. 2008.
[35] S. Pisana, M. Cantoro, A. Parvez, S. Hofmann, A. C. Ferrari, and J. Robertson, "The role of precursor gases on the surface restructuring of catalyst films during carbon nanotube growth," *Physica E-Low-Dimensional Syst. Nanostructures*, vol. 37, pp. 1–5, Mar. 2007.
[36] N. M. Rodriguez, "A review of catalytically grown carbon nanofibers," *J. Materials Res.*, vol. 8, pp. 3233–3250, Dec. 1993.
[37] C. P. Deck and K. Vecchio, "Prediction of carbon nanotube growth success by the analysis of carbon-catalyst binary phase diagrams," *Carbon*, vol. 44, pp. 267–275, Feb. 2006.
[38] W. Q. Deng, X. Xu, and W. A. Goddard, "A two-stage mechanism of bimetallic catalyzed growth of single-walled carbon nanotubes," *Nano Lett.*, vol. 4, pp. 2331–2335, Dec. 2004.
[39] N. Krishnankutty, C. Park, N. M. Rodriguez, and R. T. K. Baker, "The effect of copper on the structural characteristics of carbon filaments produced from iron catalyzed decomposition of ethylene," *Catalysis Today*, vol. 37, pp. 295–307, Aug. 1997.
[40] P. Schwalbach, S. Laubach, M. Hartick, E. Kankeleit, B. Keck, M. Menningen, and R. Sielemann, "Diffusion and isomer-shift of interstitial iron in silicon observed via in-Beam mossbauer-spectroscopy," *Phys. Rev. Lett.*, vol. 64, pp. 1274–1277, Mar. 1990.
[41] J. M. Simmons, B. M. Nichols, M. S. Marcus, O. M. Castellini, R. J. Hamers, and M. A. Eriksson, "Critical oxide thickness for efficient single-walled carbon nanotube growth on silicon using thin SiO2 diffusion barriers," *Small*, vol. 2, pp. 902–909, Jul. 2006.
[42] Y. J. Jung, B. Q. Wei, R. Vajtai, and P. M. Ajayan, "Mechanism of selective growth of carbon nanotubes on SiO2/Si patterns," *Nano Lett.*, vol. 3, pp. 561–564, Apr. 2003.
[43] A. Y. Cao, P. M. Ajayan, G. Ramanath, R. Baskaran, and K. Turner, "Silicon oxide thickness-dependent growth of carbon nanotubes," *Appl. Phys. Lett.*, vol. 84, pp. 109–111, Jan. 2004.
[44] A. Almazouzi, M. P. Macht, V. Naundorf, and G. Neumann, "Diffusion of iron and nickel in single-crystalline copper," *Phys. Rev. B*, vol. 54, pp. 857–863, Jul. 1996.
[45] O. Kononchuk, K. G. Korablev, N. Yarykin, and G. A. Rozgonyi, "Diffusion of iron in the silicon dioxide layer of silicon-on-insulator structures," *Appl. Phys. Lett.*, vol. 73, pp. 1206–1208, Aug. 1998.
[46] M. D. Groner, J. W. Elam, F. H. Fabreguette, and S. M. George, "Electrical characterization of thin Al_2O_3 films grown by atomic layer deposition on silicon and various metal substrates," *Thin Solid Films*, vol. 413, pp. 186–197, Jun. 2002.
[47] R. L. Puurunen, "Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process," *J. Appl. Phys.*, vol. 97, p. 121301, Jun. 2005.
[48] A. Rahtu, T. Alaranta, and M. Ritala, "In situ quartz crystal microbalance and quadrupole mass spectrometry studies of atomic layer deposition of aluminum oxide from trimethylaluminum and water," *Langmuir*, vol. 17, pp. 6506–6509, Oct. 2001.

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